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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Practice for Identification of Organic Compounds in Water by Combined Gas Chromatography and Electron Impact Mass Spectrometry [1]

This standard is issued under the fixed designation D 4128; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers the identification of organic compounds by gas chromatography/mass spectrometry (GC/MS) (electron impact) that are present or extracted from water and are capable of passing through a gas chromatograph without alteration. The practice is intended primarily for solutions for which 10 ng or more of any component of interest can be introduced onto a gas chromatographic column. This practice has the advantage of providing tentative identifications of volatile and semi-volatile organics, but is restricted to (*a*) compounds for which reference spectra can be obtained and (*b*) compounds that can be separated by gas chromatography (GC). These restrictions are imposed on the practice, but are not a limitation of the technique. The practice is written for, but not restricted to, analysis using automated data acquisition and handling.

1.2 Although a detection amount of 10 ng is suggested for the practice, this amount can only be considered an approximate guide. The actual detection limits for each component must be determined in each laboratory. Actual detection amounts will vary with the complexity of the sample, the kind and condition of the GC/MS system, the sample preparation technique chosen, and the application of cleanup techniques to the sample extract, if any.

1.3 The practice is applicable to the identification of many organic constituents of natural and treated waters. It includes all modes of sample introduction, including injection of organic extracts, direct aqueous injection, and purge and trap techniques.

1.4 The practice is applicable to either packed or capillary column gas chromatography, including wide-bore capillary columns. Because of their greatly enhanced resolution, capillary columns are recommended.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1066 Practice for Sampling Steam[2]

D 1129 Terminology Relating to Water[2]

D 1192 Specification for Equipment for Sampling Water and Steam[2]

D 1193 Specification for Reagent Water[2]

D 2908 Practice for Measuring Volatile Organic Matter in Water by Aqueous-Injection Gas Chromatography[3]

D 3370 Practices for Sampling Water[2]

D 3694 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents[3]

D 3871 Test Method for Purgeable Organic Compounds in Water Using Headspace Sampling[3]

D 3973 Test Method for Low-Molecular Weight Halogenated Hydrocarbons in Water[3]

D 5175 Test Method for Organohalide Pesticides and Polychlorinated Biphenyls in Water by Microextraction and Gas Chromatography[3]

D 5316 Test Method for 1,2-Dibromoethane and 1,2-Dibromo-3-Chloropropane in Water by Microextraction and Gas Chromatography[3]

D 5317 Test Method for the Determination of Chlorinated Organic Acid Compounds in Water by Gas Chromatography with an Electron Capture Detector

E 260 Practice for Packed Column Gas Chromatography[4]

E 355 Practice for Gas Chromatography Terms and Relationships[4]

2.2 *U.S. Environmental Protection Agency:*

Methods for the Determination of Organic Compounds in Drinking Water-Supplement I, EPA/600/4-90/020, July 1990[5]

Methods for the Determination of Organic Compounds in Drinking Water-Supplement II, EPA/600/R-92/129, August 1990[5]

[1] This practice is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 11.02.

[4] *Annual Book of ASTM Standards*, Vol 14.02.

[5] Available from National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, VA 22161.

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *volatile organic compound*—an organic compound that can be readily separated from water by inert gas sparging and thermally desorbed onto a GC column or is readily amenable to direct aqueous injection GC. The compounds must elute from the column within its temperature range without alteration of the structure of the compound.

3.1.2 *semi-volatile organic compound*—an organic compound that can be separated from water by extraction, either liquid/liquid or solid phase, undergo volume adjustment, and be injected onto a GC. The compounds must elute from the column within its temperature range without alteration of the structure of the compound.

3.1.3 *tentative identification*—all identifications are considered tentative until confirmed by co-injection of an authentic reference compound showing identical retention time and similar mass spectra. (Tentative identification based on library matches only are subjected to false positives.)

3.1.4 *match*—two criteria must be satisfied to verify a comparison of a sample component to a standard match: (*1*) elution of the sample component at the same retention time as the standard component as shown by co-injection or standard addition, and (*2*) correspondence of the sample component and the standard component mass spectrum. If co-elution of interfering components prohibits accurate assignment of the sample component retention time from the total ion chromatogram, the retention time should be assigned by using extracted ion current profiles for ions unique to the component of interest. To meet the second criteria, all ions present in the authentic mass spectra at a relative intensity greater than 10 % (whereas the most abundant ion in the spectrum equals 100 %) must be present in the sample spectrum; the relative intensities of these ions must agree within ± 20 % between the standard and sample spectra. (As an example, for an ion with an abundance of 50 % in the standard spectra, the corresponding sample abundance must be between 30 % and 70 %.) However, there may be additional peaks in the sample mass spectrum caused by co-eluting interfering components that are not present in the reference mass spectrum.

3.1.5 *confirmed identification*—in order to confirm a tentative identification, both the GC retention data and the mass spectrum of a compound shall uniquely match those of a reference compound as demonstrated by co-injection of the authentic standard with the tentatively identified compound.

3.1.6 *reconstructed gas chromatogram (see Note 1) (RGC)*—an RGC is the computer output representing either the summed intensities of all scanned ion intensities or a sample of the total current in the ion beam for each spectrum scan plotted against the corresponding spectrum number. Generally, it can be correlated with a flame ionization detector gas chromatogram.

NOTE 1—There are many synonyms in common use for RGC. These include: total ionization plot, total ionization current trace, reconstructed ion chromatogram, total ion current profile, and total ion chromatogram.

3.1.7 *reference compounds*—these are authentic materials used to obtain mass spectra and gas chromatographic retention data.

3.1.8 *mass chromatogram (see Note 2)*—a limited mass RGC, or mass chromatogram, represents the intensities of ion currents for only those ions having particular mass to charge ratios. It is a means of quickly scanning a complex RGC plot to locate peaks which could be specific compounds or types of compounds. However, a complete mass spectrum is required for tentative identification.

NOTE 2—There are several synonyms in current use for mass chromatogram. These includes: mass fragmentogram, extracted ion current profile, and limited mass reconstructed gas chromatogram.

3.1.9 *GC/MS/DS*—stands for gas chromatograph-mass spectrometer-data system.

3.2 *Definitions*:

3.2.1 For definitions of terms relating to water used in this practice, refer to Definitions D 1129. For definitions of terms relating to gas chromatography used in this practice, refer to Practice E 355.

4. Summary of Practices

4.1 The practice consists of the introduction of organic compounds from water into a GC/MS for mass spectral identification. Volatile organic compounds are typically introduced through a purge-and-trap sample introduction device, although volatile compounds can also be introduced by direct aqueous injection. Semi-volatile compounds are typically introduced as organic extracts from an extracted sample by syringe. A component's spectrum is recorded as the component elutes from the chromatographic column. The tentative identification of a sample component is determined based on its mass spectrum and supported by its GC retention data. This tentative identification may be confirmed by co-injection of an authentic standard yielding an identical retention time and a similar mass spectrum.

5. Significance and Use

5.1 With the common occurrence in water of organic compounds, some of which are toxic, it is often necessary to identify the specific compounds present.

6. Interferences

6.1 Sample alteration and component of interest losses are not true interferences, but are a source of trouble in doing a qualitative GC/MS analysis. Examples of component loss are: decomposition, polymerization, adsorption, and both volatilization prior to introduction into the GC and non-volatilization after introduction into the GC. In addition, GC/MS interface plugging can lead to apparent losses.

6.2 Chromatographically unresolved compounds or instrumental background which co-elutes with the compounds of interest can interfere with this practice. These interferences can change the apparent mass spectrum of the compound of interest, thereby making tentative identification difficult.

6.3 Other interferences, such as background GC peaks due to contaminated sample preparation reagent blanks, GC columns, instrumentation or column bleed, are common problems that the analyst must strive to understand and eliminate.

7. Apparatus

7.1 *GC/MS/DS*—A gas chromatograph interfaced to a mass

spectrometer having electron impact ionization capability is used. [6] Although not required, most modern GC/MS systems are typically controlled by a data system for computerized instrument control of data acquisition and data reduction. Packed or capillary GC columns may be used.

7.2 *Apparatus required to extract organic compounds from water and concentrate them in a small volume of organic solvent*—This apparatus includes a 2-L separatory funnel for batch extractions or 1-L continuous liquid-liquid extractor and facilities for Kuderna-Danish concentration. Liquid-liquid extraction for volatile organic constituents can be conducted using the apparatus specified in Test Method D 3973.

7.3 *Apparatus for purge-and-trap GC/MS sample introduction*—See Test Method D 3871 or EPA Method 524.2.

7.4 *Microsyringe*, 10-µL.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society.[7] For trace analysis using organic solvents for liquid-liquid extraction or elution from solid sorbents, solvents specified as distilled-in-glass, nano-grade, or pesticide-grade frequently have lower levels of interfering impurities.[8] In all cases, sufficient reagent blanks must be processed with the samples to ensure that all compounds of interest are not present as blanks due to reagents or glassware. Other grades of reagents may be used, providing it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification D 1193, Type II. This water must be shown to not contain contaminants at concentrations sufficient to interfere with the analysis.

8.3 *Reference compounds* shall be of known purity; impurity peaks shall not interfere with the compound of interest.

8.4 *Reference spectra* for tentative identifications may be obtained from various publications.[9] Many GC/MS/DS systems contain libraries of reference spectra as well as software required to match unknown spectra to these libraries. Libraries of compounds of interest may be generated from reference compounds run on the same instrument used for unknown analysis and under the same conditions. Such libraries should result in faster and more accurate tentative identifications than large generalized libraries. Reference spectra for confirmed identifications are determined under the same conditions for sample analysis by co-injecting the reference compounds with the sample extract, or adding the reference compounds to aqueous samples, and confirming both the co-elution of the unknown and reference compounds and their matched mass spectra.

8.5 *Gas Chromatography Column*—All-inclusive guidelines for GC column selection do not exist. Each analysis requires careful consideration of the column used (see Note 3). Bonded phase fused silica capillary columns have proven remarkably popular and successful. For examples, consult other ASTM test methods, such as Test Methods D 5175, D 5316, D 5317, or US EPA methods. Liquid phases for GC columns used in direct aqueous injection analysis shall conform to Practice D 2908.

NOTE 3—General guidelines for column selection can be found in GC suppliers' literature and textbooks, and ASTM Atomic/Molecular Data Series AMD 25A and AMD 25A S-1, Gas Chromatographic Data Compilation (and supplement), ASTM, 1971.

8.6 *Methyl Stearate*.

8.7 *Malathion*. [10]

8.8 *bis-(pentafluorophenyl)Phenyl Phosphine*.

8.9 *Isopropyl Alcohol*.

8.10 *Methylene Chloride*.

8.11 *Methyl Hexanoate*.

8.12 *N-Methyl-2-Pyrrolidone*.

9. Hazards

9.1 **Caution:** Isomeric compounds may be difficult to separate by GC and the mass spectra of isomers are frequently identical within experimental error. This could lead to either ambiguity in identification or to actual incorrect identification in some cases. The analyst must be aware of this potential problem.

9.2 **Caution:** When attempting to identify compounds in water samples containing large quantities of compounds, particularly complex mixtures such as petroleum products, great care must be exercised to determine that candidate unknown mass spectra are as devoid of interfering peaks as possible. Judicious choice of background-subtracting routines can assist in this endeavor. Additional information can be gathered by examining the extracted ion current profiles of the major mass spectral peaks in the candidate spectrum. Frequently, the occurrence of contaminated spectra can be determined by noting differences in the profiles of several mass chromatograms that do not exactly fit the profiles of the peaks of the compound of interest. These may be co-eluting in0terferences. However, it is rarely possible to completely eliminate all interferences from complex, low-level analyses, and the analyst must be aware of this in interpreting unknowns against reference spectra.

9.3 **Warning:** Due care shall be exercised in handling

[6] Consult operation manuals from manufacturers of GC/MS or GC/MS/DS systems.

[7] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[8] These products are available from most laboratory suppliers.

[9] Reference spectra are published by the American Society for Mass Spectrometry (*A Guide to Collection of Mass Spectral Data*, 2nd ed., 1978), P.O. Box 1508, East Lansing, MI 48826, the American Petroleum Institute (Project 44), 1220 "L" St., N.W., Washington, DC 20005, the National Institute of Standards and Technology, Gaithersburg, MD 20899, and Wiley Interscience, John Wiley and Sons, 605 Third Ave., New York, NY 10158.

[10] Malathion is a trademarked product from American Cyanamid, Agricultural Research Division, P.O. Box 400, Princeton, NJ 08540.

samples to minimize operator exposure to all chemicals including solvents, standards, and reagents. Solvents are a particular source of hazard because of the large quantities used in many sample preparation procedures. General practice regarding the proper use of a gas chromatograph/mass spectrometer system can be found in the manufacturer's operation manual. Since potentially toxic materials may be handled, all effluent and vent gases from any source should be vented in an environmentally safe manner. Possible sources to be considered include split gas from GC exhaust, gas from vacuum pumps, and waste containers.

10. Sample Handling, Preparation, Preservation, and Introductions

10.1 Collect the sample in accordance with Practice D 1066, Specification D 1192, Practices D 3370, or Practices D 3694.

10.2 *Sample Preparation*:

10.2.1 *Techniques of Sample Preparation*—There are many techniques of sample preparation, and the most appropriate to the application should be used.[11] Among the more widely used techniques are:

10.2.1.1 Direct aqueous injection (see Practice D 2908).

10.2.1.2 Liquid-liquid extraction (acid, base, neutral), followed by concentration adjustment and injection. Extraction of a 1-L sample is typically accomplished by methylene chloride batch extraction using either a 2-L separatory funnel or a 1-L continuous extractor at both high and low pH. Liquid-liquid extraction can also be used for volatile compounds (see Test Method D 3871).

10.2.1.3 Purge-and-trap, which consists of sparging volatile organic compounds from water with an inert gas, collecting the compounds on a trap, and then thermally desorbing them onto the head of a GC column (see Test Method D 3973 and EPA Method 524.2).

10.3 *Sample Preservation*—There may be existing methodology for preservation of specific analytes. If so, that methodology should be followed; if not, then the appropriate sections of Practices D 3694 will apply. Volatile samples will be preserved according to EPA Method 524.2.

10.4 *Sample Introduction*—Sample introduction into the chromatograph shall follow the precautions described in Practice E 260.

11. GC/MS System Performance

11.1 Depending on the sample matrix (water or organic solvent), identification of the solutes in one of the following solutions shall be used to establish the satisfactory performance of the GC/MS system before proceeding to analyze unknown solutions. The RGC generated by the test solution should give GC peaks with a signal to background ratio greater than four-to-one. A representative mass spectrum corresponding to each GC peak should be identified in accordance with criteria in use in the operator's laboratory. Such criteria should include reference to literature spectra or matching and interpreting techniques described in the literature **(1)**.[12]

Methylene chloride—methylstearate, bis−(pentafluoro−phenyl) phenyl phosphine, Malathion

Water—isopropyl alcohol, methyl hexanoate, N−methyl−2−pyrrolidone

Each component shall be present at 25 ng/µL. Inject 2 µL of either solution.

11.2 *Preparation of Performance Check Solution—Methylene Chloride Solution*:

11.2.1 Weigh 125 mg each of methyl stearate, bis-(pentafluorophenyl)phenyl phosphine, and Malathion into separate 100-mL volumetric flasks using an analytical balance accurate to 0.0001 g. Dilute each to volume with methylene chloride and mix well.

11.2.2 Pipet 2 mL of each solution into the fourth volumetric flask and dilute to volume with methylene chloride. This solution contains 25 ng/µL of each component.

11.2.3 Transfer the contents of each flask to a separate 120 mL screw cap brown glass bottle with a polytetrafluoroethylene (PTFE)-lined septum cap and store at 4°C. Storage lifetime is not known, but should be enhanced by maintaining the solutions at 4°C in the dark. Transferring approximately 1 mL of the 25 ng/L solution to a 2-mL screw-cap vial with a polytetrafluoroethylene (PTFE)-lined septum cap is convenient. This 1-mL solution can be readily replaced weekly.

11.3 *Direct Aqueous Injection Water Solution*:

11.3.1 Clean a 1-L volumetric flask with chromic acid cleaning solution.

11.3.2 Rinse thoroughly and fill with clean water to the mark.

11.3.3 Insert PTFE-covered stirring bar and chill in an ice bath for at least 40 min with stirring.

11.3.4 Inject 25 µL each of N-methyl-2-pyrrolidone, methyl hexanoate, and isopropyl alcohol into the volumetric flask below the surface of the water.

11.3.5 Stir approximately 10 min.

11.3.6 Remove the stirring bar.

11.3.7 The final concentration of each compound is as follows:

N-methyl-2-pyrrolidone = 25.7 ng/µL
Methyl hexanoate = 22.1 ng/µL
Isopropyl alcohol = 19.6 ng/µL

11.3.8 Cap the flask and seal with PTFE tape and store at 4°C. Storage lifetime is not known. Weekly preparation is recommended.

11.4 For volatile samples to be analyzed by purge-and-trap, follow the system performance procedures listed in Test Method D 3973 or EPA Method 524.2.

12. Data Acquisition

12.1 A method blank should be prepared with organic free water using the same sample preparation technique as the unknown sample. Compounds detected in the method blank

[11] Useful references for these techniques may be found in the bi-annual review issues of *Analytical Chemistry*.

[12] The boldface numbers in parentheses refer to the references at the end of this practice.